FOCAL POINT EXTRAPOLATION PROCEDURES: EXTENSION TO THE COUPLED CLUSTER SINGLES, DOUBLES, TRIPLES, AND PERTURBATIVE QUADRUPLES CCSDT(Q) LEVEL OF THEORY

by

NATHAN JOSEPH STIBRICH

(Under the Direction of Henry F. Schaefer III)

ABSTRACT

The high level of accuracy obtained with present computational chemistry methods is rapidly increasing with faster computing, more efficient codes, and higher levels of theory becoming available for general use. Chemical accuracy is within the field's grasp for most small molecules. However, some investigations warrant even higher accuracy that that. In this work, the recently implemented coupled cluster with singles, doubles, triples, and perturbative quadruples [CCSDT(Q)] level of theory is exploited under the focal point scheme to attain very accurate properties for the HCCO radical and implications for its further utility are discussed.

INDEX WORDS: Ab initio, Quantum Chemistry, Ketenyl Radical, HCCO, Coupled Cluster, CCSDT(Q)

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

The main aim of theoretical chemistry has become the prediction of molecular properties and behaviors. The predictive power available from computational methods continues to increase at a staggering rate with faster computing and more efficient codes. In addition, higher levels of theory, or more accurately, higher level approximations and larger basis sets, are becoming increasingly available. However, while these methods are available, in most cases, their computational costs can be astronomical. Therefore, many theoretical chemists strive to derive methods of approximating such theories to obtain similar accuracy at a fraction of the computational cost.

One of the most promising techniques developed so far is the focal point extrapolation procedure first expounded by Allen and coworkers.(1-5) In essence, this procedure takes advantage of the rapid, consistent convergence found in correlated energies when basis sets like Dunning's correlation consistent basis sets are used.(6-10) This property allows for the extrapolation of finite basis set results to the complete basis set (CBS) limit, thus granting nearly exact results for a given level of theory. Likewise, higher levels of theory exhibit fairly uniform convergence to the full configuration interaction (FCI) limit.

In detail, focal point analyses involve setting up a two-dimensional extrapolation grid of single-point total energies taken at accurate reference geometries in order to monitor convergence toward the CBS/FCI limit, or in other words, the exact energy within the non-relativistic Born-Oppenheimer approximation. For each level of theory, the energies are extrapolated to the CBS limit. The functional form implemented for the Hartree-Fock extrapolations is

$$E_{\mathrm{HF}}X = E^{\infty}{}_{\mathrm{HF}} + ae^{-bX},$$

while that used to extrapolate correlated energies is

$$E_{\mathrm{corr}}x = \mathrm{a} + bX^{-3},$$

which has been suggested by Helgaker, Klopper, Koch, and Noga.(11,12) Often, to save on computational cost, the focal point approach will be used with frozen-core computations. In order to correct for this, an analogous core correlation extrapolation may be implemented. Also, auxiliary corrections may be added to the focal point energies to account for Born-Oppenheimer, relativistic, and spin-orbit coupling effects.

The focal point approach has shown great success in determining numerous difficult reaction enthalpies and heats of formation. Similar principles have spawned a number of other competing approaches, such as the HEAT protocol and W*n* theories.(13-17) Both approaches are comprised of a set of fixed protocols designed to produce thermochemical predictions within a required degree of accuracy while minimizing computational cost.

More recently, however, our group has questioned whether energies are the only property which can benefit from such an approach. A few projects have explored whether slowly-converging molecular geometries might be determined in a similar vein. In a study of ortho-benzyne, a molecule for which the "gold-standard" CCSD(T)/cc-pCVQZ geometry optimization would be prohibitively expensive, a composite ($c\sim$) approach to optimizing the geometry at such a level was successfully employed.(18) In order to accomplish this, numerical gradients were calculated using single point energies of the following type:

$$E[c\sim \mathrm{CCSD(T)\text{-}AE/cc\text{-}pCVQZ} \equiv E[\mathrm{CCSD(T)\text{-}FC/cc\text{-}pVTZ}]$$
$$+\, E[\mathrm{MP2\text{-}AE/cc\text{-}pCVQZ}] - E[\mathrm{MP2\text{-}FC/cc\text{-}pVTZ}].$$

Theoretical geometries obtained from this composite approach were accurate to within 0.001 Å for bond lengths and about 0.1° for bond angles, quite comparable to full CCSD(T)/cc-pCVQZ optimizations. In that same study, the ortho-benzyne fragments acetylene and diacetylene were optimized both with the composite approach and explicit computations. The bond lengths agreed to within 0.0002 Å, lending further credence to the composite approach.

In the present work, the HCCO radical, whose properties have proven to be very sensitive to the basis set and level of theory employed. Therefore, in order to obtain the barrier to linearity, the focal point method was used. In addition, the geometry was optimized with very high levels of theory, yet convergence did not seem to have been achieved. Thus, taking advantage of the recently implemented CCSDT(Q) method,(19) the composite approach was extended in this study to the c ~ CCSDT(Q)/aug-cc-pCVQZ level of theory.

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CHAPTER 2

COMPOSITE CCSDT(Q) INVESTIGATION OF THE KETENYL RADICAL HCCO AND ITS BARRIER TO LINEARITY

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ABSTRACT

The troublesome barrier to linearity of the combustion intermediate ketenyl radical (HCCO) has been computed via focal point extrapolation through coupled cluster theory with single, double, triple, and perturbative quadruple excitations [CCSDT(Q)], utilizing the aug-cc-pVXZ (X=D,T,Q,5,6) family of basis sets. Previous theoretical treatments of HCCO have shown a very strong dependence on the correlation level and basis set employed, particularly for the CCH bond angle, leading us to define a composite approximation to all-electron (AE) CCSDT(Q)/aug-cc-pCVQZ, which is formulated within the spirit of the focal point approach. After optimizing the geometries of all species at this c~CCSDT(Q)-AE/aug-cc-pCVQZ level of theory, we further refine the energetics and monitor the performance of the composite approach by performing a full focal point analysis to account for basis set error. Auxiliary corrections such as diagonal Born-Oppenheimer corrections and relativistic effects to the barrier to linearity are included. Additionally, we compute fundamental vibrational frequencies and other spectroscopic constants through application of second-order vibrational perturbation theory (VPT2) to the full quartic force field at the CCSD(T)/aug-cc-pCVQZ level. The resulting computed (ν_2, ν_5) of (2025, 483) cm^{-1} agree very well with the experimental values, (2023, 494) cm^{-1}.

INTRODUCTION

The ketenyl (HCCO) radical was long ago recognized as a prevalent component of hydrocarbon flames(1) and is thought to have astrophysical interest as well(2,3). Thus, it has been the subject of numerous kinetic(4-13), spectroscopic(14-21), and theoretical investigations(2,22-36). By analyzing the submillimeter microwave spectrum of HCCO, Endo and Hirota determined that this molecule has a bent ground state geometry(14). More recently, two vibrational frequencies have been observed for the ground state by laser-induced fluorescence, the CCH bending mode at 494 cm^{-1} and a stretching mode at 2023 cm^{-1}(21,37).

The ground state of HCCO was first studied theoretically through CI computations by Harding in 1981, and eight years later J. D. Goddard showed that electron correlation was particularly important for this species(22,23). Szalay and coworkers subsequently applied coupled cluster methods to determine the geometry and harmonic vibrational frequencies of the bent $^2A''$ ground state of the HCCO radical. They also investigated the linear Renner-Teller counterpart $^2A'$ surface which collapses into the degenerate $^2\Pi$ state(31-33).

Several kinetic experiments on the reaction of $C_2H + O(^3P)$ have concluded that the reaction should proceed through a transition state similar to the $^2A'$ state of HCCO, or one of its vibrationally excited states(38-40). A linear transition state has also been investigated for the collisional quenching of CH(a $^4\Sigma^-$) by CO(36). While the heat of formation for the $^2A''$ ground state of HCCO has been thoroughly investigated in an important recent paper by Szalay, Tajti, and Stanton(34), the relative energy of the linear $^2\Pi$ state is still a matter of debate. Experimentally, the barrier to linearity is difficult to determine, since the $^2\Pi$ state is a transition state. However, Endo and Hirota(14) determined from pure rotational spectra that the energy barrier should be 3200 cm^{-1} if the unpaired electron is localized on the oxygen, or 540 cm^{-1} if localized on the neighboring carbon, preferring the latter assumption.

As shown in Table 2.1, theoretical determinations of the linear barrier height have varied considerably, ranging all the way from 105 cm^{-1} to 1828 cm^{-1}(26,29,30,32,33), due in large part to the strong dependence of ketenyl radical computations on electron correlation(32) and the AO basis set employed(29). With DZP MR-CI computations, Kim and Shavitt(26) predicted the barrier to be 981 cm^{-1}. Szalay *et al.*(31,32) analyzed the HCCO wavefunction using EOMIP-

CCSD with a TZ2P basis and concluded that the unpaired electron was delocalized, with substantial density on both the oxygen and carbon, estimating the energy barrier at 1175 cm^{-1}. More recently, Schafer-Bung, Engels, Taylor, Neumark, Botschwina, and Perić performed UCCSD(T) computations with large basis sets and recorded the photoelectron spectrum of the anion HCCO$^-$, which together suggested that the barrier to linearity be restricted to a value between 700 and 900 cm^{-1}(30). Therefore, the current study extends past investigations to more accurately determine the barrier height to linearity for this radical.

COMPUTATIONAL METHODS

The full quartic force field of bent ^{2}A" HCCO was computed at the highly accurate all-electron coupled cluster singles, doubles, and perturbative triples [CCSD(T)] level using the large core-valence polarized, quadruple zeta (aug-cc-pCVQZ) augmented basis set of Woon and Dunning(41,42). For the C and O atoms, the aug-cc-pCVQZ basis is a [16*s*10*p*6*d*4*f*2*g* / 9*s*8*p*6*d*4*f*2*g*] set, and for HCCO it consists of 373 contracted gaussian functions.

To obtain accurate fundamental frequencies, anharmonic contributions were computed from the third and fourth derivatives of the molecular energy with respect to nuclear coordinates. These higher order derivatives are determined by numerical differentiation of tightly converged energies at a large number of displaced geometries. The internal coordinates were chosen as

$$\begin{aligned}
S_1 &= r(\mathrm{H-C}) \\
S_2 &= r(\mathrm{C-C}) \\
S_3 &= r(\mathrm{C-O}) \\
S_4 &= \theta(\mathrm{H-C-C}) \\
S_5 &= \alpha_x(\mathrm{H-C-C-O}) = \sin(\rho)\cos(\tau) \\
S_6 &= \alpha_y(\mathrm{H-C-C-O}) = \sin(\rho)\sin(\tau)
\end{aligned}$$

where r is the bond length between two connected atoms, θ is the valence bond angle, and τ is the molecular torsional angle. The linear bending coordinates α_x and α_y deflect complications arising from the nearly linear CCO bond angle and were shown to be very useful in a study of the geometrically similar HNCO molecule(43).

To span the full quartic force field required 263 energies at displaced geometries. For sufficient numerical precision, each energy was converged to 10^{-11} E_h. Vibrational anharmonicities were computed by application of second-order perturbation theory(43-50) (VPT2) to the quartic force field. The *Mathematica*(51) program INTDIF2005(52,53) was used to compute the force constants in internal coordinates, while INTDER2005(54-57) was used to perform a nonlinear transformation to the Cartesian space, and the ANHARM(55,58) program was run for the VPT2 analysis.

As the ketenyl radical's barrier to linearity has proven to depend strongly on the basis set and theoretical method employed(32,33), this study extends the theoretical investigation of the ketenyl radical in its two lowest electronic states, the Renner-Teller pair of ^{2}A" and $^2\Pi(^2$A'), to very high level coupled cluster computations. An extrapolation of the energy barrier was implemented via the focal point scheme of Allen and coworkers(59-63).

Optimized geometries were determined with large-basis CCSD and CCSD(T) computations. Due to the flexibility of the HCC bond angle, higher level correlation effects were included by utilizing a composite approximation to the all-electron CCSDT(Q) level. Herein, this approximation is defined as

$$E_{\text{c\sim CCSDT(Q)}}^{\text{aug-cc-pCVQZ}} = E_{CCSD(T)}^{aug-cc-pCVQZ} + E_{CCSDT(Q)}^{cc-pVDZ} - E_{CCSD(T)}^{cc-pVDZ}.$$

The geometry at the c~CCSDT(Q)/aug-cc-pCVQZ level of theory (Table 2.2) was optimized for each of the Renner-Teller states and used in all the focal point energy computations. While the focal point procedure has been described in detail in previous publications, a brief outline is given. The energies were determined under the frozen-core approximation at the ROHF(64), ZAPT2 (second-order Z-averaged perturbation theory)(65), CCSD, CCSD(T)(70,71), and CCSDT (coupled cluster through full triple excitations) levels of theory with Dunning's augmented valence correlation consistent basis sets , denoted aug-cc-pVXZ (X = D, T, Q, 5, 6)(68-70). For each level of theory, the energies were extrapolated to the complete basis set limit. The functional form implemented for the Hartree-Fock extrapolations is

$$E_{\mathrm{HF}}X = E^{\infty}{}_{\mathrm{HF}} + ae^{-bX},$$

while that used to extrapolate correlated energies is

$$E_{\mathrm{corr}}X = \mathrm{a} + bX^{-3},$$

as suggested by Helgaker, Klopper, Koch, and Noga(71,72). Perturbative quadruple excitations, calculated with the MRCC code for CCSDT(Q)(73,74) interfaced with the ACES II program suite, were also included. At present, this code can only utilize unrestricted Hartree-Fock references for CCSDT(Q); however, as the full CI limit is closely approximated at this level, the choice of reference wavefunction is far less important. Nevertheless, an estimate of the effect of this change was included using the formula

$$E_{\mathrm{ROCCSDT(Q)}} = E_{\mathrm{ROCCSDT}} + [E_{\mathrm{UCCSDT(Q)}} - E_{\mathrm{UCCSDT}}],$$

where the subscript ROCCSDT denotes the energy obtained starting from ROHF wavefunctions, while UCCSDT and UCCSDT(Q) denote calculations with UHF wavefunctions.

The massively parallel quantum chemistry package (MPQC)(75) allowed for parallel, direct computation of the ZAPT2 energies, which are free from spin contamination, in contrast to other open-shell perturbation theory formulations(65,76). The CCSD and CCSD(T) computations were performed with the MOLPRO program suite(77), while the CCSDT and

CCSDT(Q) energies were determined using the Mainz-Austin version of the ACES II program suite(78,79). The core orbitals were frozen in the computations employing the aug-cc-pVXZ basis sets, consistent with basis set design; however, the assumption that these perform better in the frozen-core approximation has been challenged(80). Core correlation effects were included with all-electron computations at the CCSD(T) level of theory with the core-valence basis set aug-cc-pCVQZ(42).

To determine the barrier height to linearity with even greater precision, a number of other often important corrections were considered. Zero-point vibrational energy (ZPE) corrections can be rather significant. However, one of the modes for the linear state of HCCO is imaginary, because it describes the reaction coordinate involved in the inversion between the trans-bent and linear HCCO forms. This mode might be excluded from the ZPE, giving both states the same number of modes in their ZPE determinations, but Renner-Teller coupling in the transition state makes this a dubious proposition. Thus, the ZPE correction is not justified in such cases and was excluded from the present determination. Non-Born-Oppenheimer effects were included using the diagonal Born-Oppenheimer correction (DBOC)(81,82) computed at the aug-cc-pVTZ ROHF level, since the DBOC for relative energies changes little beyond the Hartree-Fock level(83,84). Scalar relativistic corrections were included at the aug-cc-pVTZ CCSD(T) level using the one-electron Darwin and mass-velocity terms(85), which have been shown to be quite accurate for systems with first and second row atoms(86-88).

RESULTS AND DISCUSSIONS

Geometry and Vibrational Frequencies

The ground state geometries (Tables 2.2 and 2.3) optimized at the CCSD and CCSD(T) levels show that geometry optimizations of HCCO are particularly susceptible to basis set and theory choice. Optimizations using only CCSD overshoot the CCH bond angle by 1-2° and underestimate all of the bond lengths, particularly the C-O bond length where CCSD gives a value nearly 0.01 Å smaller than CCSD(T). As a measure of the quality of our geometrical parameters, we optimized the linear geometry at the cc-pCV5Z level. In general, the bond lengths at the aug-cc-pCVQZ level agree to within 0.001 Å, compared to those computed with the larger basis set. For the bent geometry, note that the CCO bond angle exhibits very little deviation upon basis set change, while the CCH bond angle has previously been noted for its extremely flat potential energy surface, which makes a small amount of uncertainty in this value relatively unimportant from an energetic standpoint(32). However, since the equilibrium geometries of bent and linear HCCO do not seem to have been fully converged upon even at rather high levels of theory, the composite optimization discussed above was utilized. We used both the composite c~CCSDT(Q)/aug-cc-pCVQZ and the explicit CCSD(T)/aug-cc-pCVQZ optimized geometries for the focal point analysis. These geometries have similar bond lengths, mostly within 0.002 Å; however, their HCC bond angles differ significantly, by nearly a full degree.

As a measure of the quality of our geometries, we note the vibrational frequencies and rotational constants computed in this study (Tables 2.4 and 2.5). At the aug-cc-pCVQZ CCSD(T) level, most of the harmonic frequencies for the ground state are significantly lower than those computed previously by Szalay *et al.*(34), except in the case of the CCH bending mode. In the Szalay paper, anharmonic corrections were made at the cc-pVTZ ROHF-CCSD(T) level to obtain theoretical fundamental frequencies. In this study, we computed anharmonic corrections for the bent ground state of HCCO using second-order vibrational perturbation theory, and achieved excellent agreement with the experimentally observed frequencies at 2023 and 494 cm^{-1}(21,37). The full quartic force field of HCCO, with all quadratic, cubic, and quartic terms, as well as anharmonicity and vibration-rotation interaction constants in internal coordinates is reported in Tables 2.6-2.10. No vibrational frequencies were computed for the composite geometry optimization; however, rotational constants were determined for both the explicit CCSD(T) and composite CCSDT(Q) geometries. The equilibrium rotational constants were corrected via an explicit consideration of the vibration-rotation interaction constants as well as the centrifugal distortion constants obtained from the quartic force field under the vibrational perturbation theory framework. When compared with experimental values, it is perhaps surprising that the explicit CCSD(T) optimization has outperformed our composite CCSDT(Q) approach. While CCSD(T)/aug-cc-pCVQZ is well-known as the computational "gold standard," CCSDT(Q) energies are known to be highly accurate(89). Perhaps, however, the low quality basis set (cc-pVDZ) used for the CCSDT(Q) energies in our formulism is too small.

Energetics

To demonstrate the effectiveness of the focal point scheme, a few features of Tables 2.11-2.13 bear examination. The CCSD(T) relative energies converge to within 0.01 kcal mol^{-1} at the 6Z level, which means that the focal point extrapolation has accomplished its first objective, recovering basis set errors. Since the correction at CCSDT changes very little from the DZ to the TZ basis, calculations beyond TZ would be superfluous, and additivity was assumed for larger basis sets. Additionally, as the perturbative quadruples correction is only 0.1 kcal mol^{-1}, the focal point procedure has succeeded in recovering the correlation energy, its second objective.

Although in this case, very high level computations were possible, a note should be made of some interesting features that might make future investigations less computationally expensive. The extrapolated ZAPT2 energy comes remarkably close to the extrapolated CCSDT values, presumably due to a fortuitous cancellation of errors. Also, the estimate of the core correction found using the relation,

$$\Delta E_{\text{core}} \approx E^{AE-CCSD(T)}_{aug-cc-pCVQZ} - E^{FC-CCSD(T)}_{aug-cc-pCVQZ}\,,$$

was -0.23 kcal mol^{-1}. While this approximation runs counter to the basis set design, this estimated core correction is within 0.03 kcal mol^{-1} of that computed from the full focal point analysis of the core correction. Thus, even in the present study, such an estimate should suffice.

Since we are comparing two high level geometry optimizations in this study, it is interesting to note the similarities between the focal point tables for each geometry. Their final relative energies are extremely close, within 0.01 kcal mol^{-1}, which is very encouraging. This lends credence to one of the assumptions of the focal point approach; namely, that focal point extrapolations can attain highly accurate energies even when one uses geometries optimized at slightly lower levels. Looking closely, the only major difference between the tables lies in the values in the DZ row. This suggests that, even though DZ relative energy increments are reliable, the DZ basis sets are perhaps insufficient by themselves for sensitive properties like geometries, which again may account for the slight inaccuracy in our composite geometry optimization.

The focal point limit for the barrier height in the valence only determination was 2.09 kcal mol^{-1}, while the core correlation correction to the barrier height was -0.23 kcal mol^{-1}. Since the UHF-CCSDT and ROHF-CCSDT relative energies differ by only 1 cm^{-1}, no significant error is expected from our switch to UHF at the CCSDT(Q) level. The small post-CCSDT correction of 0.11 kcal mol^{-1} demonstrates excellent convergence towards the full CI limit. Considerations of relativistic effects and the diagonal Born-Oppenheimer correction affect the barrier by less than 0.1 kcal mol^{-1}, yielding a total linear barrier of 1.8 ± 0.1 kcal mol^{-1} or 630 ± 30 cm^{-1}. The inclusion of higher than perturbative quadruple excitations is not expected to add more than another 20 cm^{-1}. The barrier to linearity was narrowed down to the range of 700 – 900 cm^{-1} by Schäfer-Bung *et al*(30) by comparing simulated photoelectron spectra with the experimental spectrum of $HCCO^-$. Their simulations utilized carefully chosen computed geometries for the neutral and anionic HCCO determined at high levels of theory, fit with two proposed values for the barrier to linearity at 643 and 981 cm^{-1}. Our computed value agrees quite well with the lower end of their range of energies. However, our value should be viewed as a vibrationless barrier suitable for fitting spectroscopic (Renner-Teller) levels via full dimensional variational vibrational computations.

CONCLUSIONS

In this study the geometry and barrier to linearity for the HCCO radical has been determined by high level *ab initio* quantum chemistry. A full quartic force field has also been computed to determine accurate HCCO fundamental frequencies that agree very well with experiment. The focal point extrapolation procedure used is particularly helpful in thermodynamic computations where the energy is highly dependent on the basis size and methods employed. Even for troublesome open-shell species like the ketenyl radical, highly accurate thermochemical constants have been obtained.

Including correlation contributions up to CCSDT(Q) and a number of auxiliary effects, the barrier to linearity of the ketenyl radical has now been narrowed down to the range between 650-700 cm^{-1} by both theory and experiment(30). This low barrier, in combination with the highly accurate heat of formation of the ground state of HCCO determined by Szalay et al.(34), has implications for the proposed linear transition state in the reaction of $C_2H + O(^3P)$ resulting in $CH(X\ ^2\Pi)$ or $CH(A\ ^2\Delta) + CO$(38).

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TABLES

Table 2.1. Theoretical and experimental barriers to linearity for the ketenyl radical.

Method	AO basis	Correlated	ΔE (cm^{-1})
MCSCF/MR-CI[a]	DZP	val	981
CASSCF[b]	DZP	val	1609
RCCSD(T)[b]	DZP	val	1428
UHF[c]	DZP	all	105
	TZ2P	all	126
MBPT2[c]	DZP	all	1828
	TZ2P	all	1512
UHF-CCSD[c]	DZP	all	958
	TZ2P	all	786
	cc-pVTZ	all	403
UHF-CCSD(T)[c]	DZP	all	1302
	TZ2P	all	1096
	cc-pVTZ	all	643
EOMIP-CCSD[c]	TZ2P	all	656
	cc-pVTZ	all	268
RHF-UCCSD[d]	cc-pVQZ	val	509
	aug-cc-pVQZ	val	509
	cc-pV5Z	val	485
	aug-cc-pV5Z	val	489
RHF-UCCSD(T)[e]	cc-pVQZ	val	712
	cc-pCVQZ	all	637
RHF-UCCSD(T)[d]	aug-cc-pVQZ	val	712
	cc-pV5Z	val	687
	aug-cc-pV5Z	val	690
	aug-cc-pCVQZ	all	638
CBS CCSDT(Q)[d]		all	630
Experimental[e]			700-900

[a] Kim and Shavitt(26)
[b] Schäfer et al.(29)
[c] Szalay et al.(32,33)
[d] This research
[e] Schäfer-Bung et al.(30)

Table 2.2. Optimized geometries for the ground $^{2}A''$ bent form of HCCO. Bond lengths are given in angstroms, and angles in degrees. Geometries used for focal point extrapolations are in bold.

$^{2}A''$		Electrons correlated	r_{HC}	r_{CC}	r_{CO}	∠CCH	∠CCO	
CCSD	cc-pVQZ	val	1.0696	1.2951	1.1639	134.75	169.96	a
	cc-pV5Z	val	1.0693	1.2942	1.1633	134.90	170.03	a
	aug-cc-pVQZ	val	1.0700	1.2956	1.1643	134.62	169.89	a
	aug-cc-pV5Z	val	1.0694	1.2943	1.1634	134.88	170.02	a
CCSD(T)	cc-pVTZ	val	1.0738	1.3072	1.1760	131.92	168.55	c
	cc-pVQZ	val	1.0729	1.3030	1.1725	132.69	168.92	c
	cc-pV5Z	val	1.0727	1.3021	1.1720	132.79	168.97	a
	aug-cc-pVTZ	val	1.0748	1.3080	1.1764	131.68	168.54	c
	aug-cc-pVQZ	val	1.0734	1.3035	1.1730	132.58	168.84	a
	aug-cc-pV5Z	val	1.0729	1.3023	1.1722	132.75	168.95	a
	cc-pCVQZ	all	1.0709	1.2975	1.1710	134.10	169.30	c
	aug-cc-pCVQZ	**all**	**1.0713**	**1.2981**	**1.1713**	**133.82**	**169.20**	a
c~CCSDT(Q)	**aug-cc-pCVQZ**	**all**	**1.0720**	**1.3006**	**1.1726**	**133.10**	**168.92**	a

a. This research
b. Szalay et al. with UHF wavefunctions (Ref. 34)
c. Schafer-Bung et al. (Ref. 30)

Table 2.3. Optimized geometries for the linear $^2\Pi$ stationary point of HCCO. Bond lengths are given in angstroms. Geometries used for focal point extrapolations are in bold.

$^2\Pi$		Electrons correlated	r_{HC}	r_{CC}	r_{CO}	
CCSD	cc-pVQZ	val	1.0597	1.2585	1.1767	a
	cc-pV5Z	val	1.0595	1.2579	1.1761	a
	aug-cc-pVQZ	val	1.0599	1.2588	1.1771	a
	aug-cc-pV5Z	val	1.0595	1.2580	1.1761	a
CCSD(T)	cc-pVTZ	val	1.0617	1.2653	1.1895	c
	cc-pVQZ	val	1.0616	1.2628	1.1856	c
	cc-pV5Z	val	1.0614	1.2621	1.1850	a
	aug-cc-pVTZ	val	1.0625	1.2659	1.1901	c
	aug-cc-pVQZ	val	1.0619	1.2631	1.1861	c
	aug-cc-pV5Z	val	1.0615	1.2623	1.1852	a
	cc-pCVQZ	all	1.0604	1.2600	1.1834	c
	cc-pCV5Z	all	1.0601	1.2593	1.1828	a
	aug-cc-pCVQZ	**all**	**1.0606**	**1.2603**	**1.1839**	a
c~CCSDT(Q)	**aug-cc-pCVQZ**	**all**	**1.0608**	**1.2612**	**1.1853**	a

a. This research
b. Szalay et al. with UHF wavefunctions (Ref. 34)
c. Schafer-Bung et al. (Ref. 30)

Table 2.4. Harmonic and fundamental vibrational frequencies (cm^{-1}) computed for the ground $^2A''$ and linear $^2\Pi$ states of HCCO at the CCSD(T)/aug-cc-pCVQZ level and experimental values(20,37). Symmetry assignments are made for the ground state, with the analogous linear frequencies for comparison.

		$^2A''$				$^2\Pi$
Mode	Description	ω	Δ	ν	Experiment	ω
$\nu_1(a')$	CH stretch	3339	-127	3212		3463
$\nu_2(a')$	CO stretch	2066	-41	2025	2023	2083
$\nu_3(a')$	CC stretch	1235	-6	1229		1289
$\nu_4(a')$	CCO bend	563	-12	550		556
$\nu_5(a')$	CCH bend	511	-28	483	494	511
$\nu_6(a'')$	torsion	493	25	519		405
						397i

Table 2.5. Rotational constants for the HCCO radical in MHz. The third column uses corrections from the quartic force field analysis performed at the conventional CCSD(T)/aug-cc-pCVQZ level. Experimental values are taken from Endo and Hirota(14).

	CCSD(T)/aug-cc-pCVQZ	c~CCSDT(Q)/aug-cc-pCVQZ	Experiment
		HCCO	
A_0	1191253	1160342	1243000(45000)
B_0	10885	10865	10896.788(41)
C_0	10756	10733	10766.466(39)
D_N	0.003760		0.003861(21)
D_{NK}	0.253548885		0.2376(26)
D_K	11046		18480(1200)
		DCCO	
A_0	719027	679197	652100(3600)
B_0	9910	9879	9926.8008(104)
C_0	9743	9703	9755.2316(126)
D_N	0.0034899		0.0035088(34)
D_{NK}	-1.6623		-1.6724(123)
D_K	4576		5000 (fixed)

Table 2.6. Quadratic force constants for the HCCO radical. All force constant units are consistent with energies in aJ, distances in Å, and angles in radians.

Ij	RHF	CCSD	CCSD(T)
11	6.2619	6.0834	6.0614
21	-0.1174	-0.1164	-0.1174
22	10.0587	9.6643	9.6641
31	-0.0507	-0.0399	-0.0419
32	1.7364	1.6543	1.4855
33	14.5224	14.3983	14.3633
41	0.1879	0.1621	0.1599
42	0.8579	0.7366	0.7086
43	-0.2987	-0.2653	-0.2410
44	0.2009	0.2127	0.2225
51	0.0326	0.0385	0.0394
52	0.4872	0.4418	0.4374
53	0.1102	0.1329	0.1362
54	-0.0240	-0.0453	-0.0513
55	0.8646	0.7188	0.6803
66	0.6569	0.5141	0.4841
ω_1			3339
ω_2			2066
ω_3			1235
ω_4			563
ω_5			511
ω_6			493

Table 2.7. Cubic force constants for the HCCO radical. All force constant units are consistent with energies in aJ, distances in Å, and angles in radians.

ijk	RHF	CCSD	CCSD(T)	*ijk*	RHF	CCSD	CCSD(T)
111	-34.848	-34.625	-34.628	511	-0.003	0.007	0.012
211	-0.005	0.026	0.034	521	0.015	0.040	0.040
221	-0.508	-0.484	-0.471	522	0.283	0.151	0.093
222	-61.961	-58.456	-58.161	531	-0.064	-0.059	-0.058
311	0.144	0.114	0.089	532	-0.389	-0.397	-0.401
321	0.110	0.085	0.067	533	-0.112	-0.061	-0.085
322	-2.710	-4.308	-4.266	541	-0.027	-0.028	-0.028
331	-0.116	-0.027	-0.005	542	0.090	0.037	0.020
332	-2.065	0.059	-0.200	543	0.039	0.017	0.007
333	-108.169	-107.165	-106.393	544	-0.383	-0.323	-0.305
411	0.048	0.009	0.010	551	-0.060	-0.066	-0.070
421	-0.055	-0.078	-0.102	552	-1.103	-1.004	-1.009
422	0.278	-0.004	-0.113	553	-1.110	-1.170	-1.194
431	-0.051	-0.047	-0.044	554	-0.007	-0.029	-0.029
432	0.102	0.066	0.063	555	-0.734	-0.660	-0.645
433	0.245	0.164	0.214	661	-0.053	-0.072	-0.078
441	-0.325	-0.291	-0.278	662	-0.932	-0.845	-0.837
442	-0.253	-0.326	-0.306	663	-0.979	-1.034	-1.033
443	-0.101	-0.027	-0.010	664	0.056	0.075	0.084
444	-0.497	-0.468	-0.491	665	-0.390	-0.388	-0.370

Table 2.8. Quartic force constants for the HCCO radical. All force constant units are consistent with energies in aJ, distances in Å, and angles in radians.

ijkl	RHF	CCSD	CCSD(T)	*ijkl*	RHF	CCSD	CCSD(T)
1111	135.69	164.69	176.75	5332	-8.08	-2.96	-0.50
2111	19.82	5.28	-1.49	5333	9.97	3.40	0.49
2211	-29.91	-10.68	-1.29	5411	-3.50	-1.02	0.07
2221	20.15	5.92	-1.21	5421	26.98	9.05	0.05
2222	210.56	248.74	271.93	5422	-2.32	-0.30	0.95
3111	21.29	6.34	0.22	5431	26.68	7.92	0.11
3211	-14.14	-4.30	0.09	5432	26.61	8.55	-0.33
3221	-14.05	-3.80	0.42	5433	-3.50	-1.00	0.04
3222	41.14	28.15	16.54	5441	-1.73	-0.53	0.01
3311	-28.73	-8.58	-0.42	5442	-2.58	-1.34	-0.64
3321	-14.60	-5.15	-0.66	5443	-1.47	-0.22	0.35
3322	-32.36	-21.65	-8.98	5444	1.44	0.61	0.15
3331	21.86	7.17	1.02	5511	-7.19	-2.18	-0.14
3332	20.80	20.36	11.87	5521	-3.59	-1.16	0.02
3333	566.70	588.17	604.05	5522	-7.73	-2.34	0.55
4111	10.21	2.74	-0.41	5531	-3.49	-0.89	0.05
4211	-6.84	-2.17	0.20	5532	-1.14	1.10	2.08
4221	-7.28	-2.16	0.22	5533	-7.20	-1.85	0.51
4222	12.94	5.80	1.48	5541	-1.80	-0.56	-0.03
4311	-7.22	-2.21	-0.08	5542	-2.06	-1.06	-0.43
4321	53.42	16.77	-0.10	5543	-2.17	-0.87	-0.28
4322	-7.27	-3.36	-1.29	5544	-1.85	-0.59	0.02
4331	-7.05	-2.05	0.01	5551	2.83	0.92	0.17
4332	-8.15	-2.33	0.34	5552	4.41	2.45	1.36
4333	11.25	2.65	-0.62	5553	3.77	1.92	1.10
4411	-7.01	-2.03	0.09	5554	1.33	0.39	-0.07
4421	-3.04	-0.77	0.38	5555	2.99	4.11	4.75
4422	-5.91	-1.95	0.52	6611	-7.15	-2.13	-0.15
4431	-3.66	-1.08	-0.01	6621	-3.69	-1.38	-0.23
4432	-4.32	-1.49	-0.13	6622	-9.84	-4.40	-1.51
4433	-6.85	-2.06	-0.13	6631	-3.49	-0.96	0.04
4441	3.13	1.30	0.48	6632	-1.59	0.47	1.59
4442	0.66	-0.40	-1.19	6633	-7.11	-1.84	0.51
4443	3.83	1.65	0.73	6641	-1.77	-0.51	0.01
4444	-2.14	-0.68	0.04	6642	-2.04	-0.81	-0.11
5111	10.63	3.08	0.02	6643	-1.96	-0.72	-0.17
5211	-7.03	-2.21	0.13	6644	-1.69	-0.47	0.08
5221	-7.10	-2.27	0.08	6651	-1.72	-0.52	-0.03
5222	10.39	3.89	-0.19	6652	-1.27	-0.21	0.46
5311	-7.21	-2.21	-0.10	6653	-1.21	0.01	0.59
5321	53.36	16.64	0.04	6654	-1.10	-0.35	-0.01
5322	-5.23	-0.89	1.06	6655	-0.92	0.01	0.59
5331	-7.04	-1.99	-0.02	6666	1.45	3.17	3.80

Table 2.9. Anharmonicity constants χ_{ij} in cm^{-1} for HCCO, computed at the AE-CCSD(T)/cc-pCVQZ level using vibrational perturbation theory.

	HCCO	DCCO	H^{13}CCO	HC^{13}CO	HCC^{18}O
χ_{11}	-63.241	-34.342	-62.749	-63.254	-63.241
χ_{21}	-1.785	-8.164	-2.509	-3.201	-4.245
χ_{22}	-14.227	-13.8	-14.296	-13.438	-13.672
χ_{31}	-6.266	-3.297	-7.472	-8.095	-7.015
χ_{32}	-11.693	-10.236	-10.477	-8.022	-10.647
χ_{33}	-4.678	-5.728	-4.542	-4.782	-4.155
χ_{41}	11.15	6.371	9.867	13.298	12.103
χ_{42}	-2.977	-6.664	-4.439	-0.171	-1.319
χ_{43}	11.998	18.087	14.779	7.764	13.794
χ_{44}	-11.34	-7.856	-10.163	-14.754	-13.519
χ_{51}	0.077	-2.73	0.661	-2.2	-0.887
χ_{52}	1.251	-9.873	0.962	-0.087	1.411
χ_{53}	4.511	6.526	5.612	3.753	4.278
χ_{54}	-39.483	33.465	-39.129	-37.429	-39.66
χ_{55}	-11.221	-0.62	-12.572	-7.495	-9.593
χ_{61}	-3.835	7.133	-3.808	-3.832	-3.819
χ_{62}	-9.505	-0.958	-9.383	-8.792	-9.451
χ_{63}	7.884	3.557	8.894	6.168	8.873
χ_{64}	40.043	-26.264	41.413	32.334	37.176
χ_{65}	22.686	4.948	20.125	29.88	25.445
χ_{66}	-1.687	-9.709	-1.951	-1.356	-1.89

Table 2.10. Vibration-rotation interaction constants (10^{-3} cm^{-1}) for HCCO, derived from the AE-CCSD(T)/cc-pCVQZ anharmonic force field.

	HCCO	DCCO	$H^{13}CCO$	$HC^{13}CO$	$HCC^{18}O$
α_1^A	3866	2310	3740	3819	3862
α_2^A	413.2	-78.93	330.7	381.2	597.0
α_3^A	1627	855.9	1605	1641	1473
α_4^A	-48173	-18872	-50054	-43115	-45848
α_5^A	-98350	14118	-91103	-81861	-94867
α_6^A	128509	-4231	123621	107129	122706
α_1^B	0.429	0.171	0.429	0.427	0.396
α_2^B	2.494	2.212	2.400	2.402	2.368
α_3^B	0.948	0.654	0.921	0.944	0.880
α_4^B	-0.288	-0.082	-0.396	-0.099	-0.208
α_5^B	-1.113	-0.669	-1.046	-0.998	-0.955
α_6^B	0.212	0.144	0.216	-0.018	0.050
α_1^C	0.854	0.712	0.825	0.854	0.780
α_2^C	2.483	2.119	2.382	2.390	2.377
α_3^C	1.111	0.845	1.076	1.111	1.013
α_4^C	-0.194	0.070	-0.285	-0.112	-0.162
α_5^C	0.195	-1.094	0.196	0.148	0.169
α_6^C	-1.213	0.390	-1.155	-1.182	-1.142

Table 2.11. Frozen core extrapolation for the linear barrier height of HCCO (geometries optimized at the CCSD(T)/aug-cc-pCVQZ level). Extrapolated values are denoted by brackets. All energies are given in kcal mol^{-1}. For correlated methods, the symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory. The final prediction is boldfaced.

Basis	E (HF)	+δ(ZAPT2)	+δ(CCSD)	+δ[CCSD(T)]	+δ(CCSDT)	+δ[CCSDT(Q)]	=	E [CCSDT(Q)]
DZ	1.86	1.66	-0.48	0.67	0.07	0.10		3.88
TZ	1.11	1.17	-0.58	0.60	0.07	[0.10]		2.47
QZ	1.11	0.92	-0.59	0.59	[0.07]	[0.10]		[2.20]
5Z	1.10	0.85	-0.57	0.59	[0.07]	[0.10]		[2.14]
6Z	1.1	0.81	-0.56	0.59	[0.07]	[0.10]		[2.11]
∞	[1.1]	[0.76]	[-0.55]	[0.59]	[0.07]	[0.10]		**[2.08]**
function	exp	X(-3)	X(-3)	X(-3)	Additive	Additive		fp limit
fit points; x =	(4, 5, 6)	(5, 6)	(5, 6)	(5, 6)				

Table 2.12. Frozen core extrapolation for the linear barrier height of HCCO (geometries optimized at the c~CCSDT(Q)/aug-cc-pCVQZ level). Refer to Table 2.11 for other details.

Basis	E (HF)	+δ(ZAPT2)	+δ(CCSD)	+δ[CCSD(T)]	+δ(CCSDT)	+δ[CCSDT(Q)]	=	E [CCSDT(Q)]
DZ	1.85	1.72	-0.50	0.70	0.07	0.11		3.94
TZ	1.08	1.21	-0.60	0.62	0.07	[0.11]		[2.49]
QZ	1.07	0.96	-0.61	0.61	[0.07]	[0.11]		[2.21]
5Z	1.06	0.89	-0.59	0.61	[0.07]	[0.11]		[2.15]
6Z	1.06	0.85	-0.58	0.61	[0.07]	[0.11]		[2.12]
∞	[1.06]	[0.80]	[-0.56]	[0.61]	[0.07]	[0.11]		**[2.09]**
function	exp	X(-3)	X(-3)	X(-3)	Additive	Additive		fp limit
fit points; x =	(4, 5, 6)	(5, 6)	(5, 6)	(5, 6)				

Table 2.13. Core correlation correction extrapolation for the linear barrier height of HCCO. Refer to Table 2.11 for other details.

Basis	+δ(ZAPT2)	+δ(CCSD)	+δ[CCSD(T)]	+δ(CCSDT)	=	δE (CCSDT)
DZ	0.015	-0.044	-0.006	0.000		-0.034
TZ	-0.110	-0.036	-0.001	[0.000]		[-0.147]
QZ	-0.167	-0.037	-0.001	[0.000]		[-0.204]
5Z	-0.199	-0.030	-0.002	[0.000]		[-0.232]
∞	[-0.234]	[-0.023]	[-0.004]	[0.000]		**[-0.261]**
function	X(-3)	X(-3)	X(-3)	Additive		fp limit
fit points; x =	(4, 5)	(3, 4)	(3, 4)			

CHAPTER 3

CONCLUDING REMARKS

In this work the effectiveness of the focal point approach was confirmed for calculating the barrier to linearity of the HCCO radical. A composite geometry optimization was formulated to approximate the CCSDT(Q)-AE/aug-cc-pCVQZ level of theory. In comparison with the conventional CCSD(T)-AE/aug-cc-pCVQZ geometry, it surprisingly showed slightly less agreement with experiment. One possible explanation may lie in the use of a DZ size basis to calculate the (Q) – (T) correlation correction. A full quartic force field has also been computed to determine accurate fundamental frequencies for the HCCO radical, and these agree very well with experiment. The focal point extrapolation procedure performed extremely well in evaluating the barrier to linearity of HCCO, a property for which the energy is highly dependent on the basis size and methods employed. Including correlation contributions up to the CCSDT(Q) level and the important auxiliary effects, the barrier to linearity of the ketenyl radical was predicted to be 630 cm^{-1}.